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**Catalytic Processes for Space Station
Waste Conversion**

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FOREWORD

This report documents a six-month study of a catalytic technique for processing waste products on board spacecraft. The program was funded by NASA Ames Research Center, Moffett Field, Calif., under contract NAS2-12265. Mr. F. V. Frasca was Contracting Officer, and Ms. C. C. Johnson was the technical monitor.

AiResearch Manufacturing Company, Torrance, Calif., was the contractor to NASA. AiResearch was responsible for the performance of the overall program and the systems evaluation. Dr. R. A. Madsen was the principal investigator at AiResearch. The coker and oxidizer process definition and laboratory experiments were conducted by Signal Research Center, Inc., Des Plaines, Ill. This organization is a sister company of AiResearch through the Allied-Signal Corporation. Dr. M. W. Schoonover was the principal investigator at Signal Research Center.

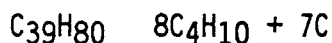
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1. INTRODUCTION AND SUMMARY

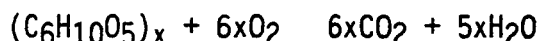
The objective of the study was to evaluate catalytic techniques for processing waste products on board space vehicles. Two basic conversion processes were considered: coking and oxidation. The waste composition and generation rate considered are defined by Wydeven (1983) for a controlled ecological life support system (CELSS). In the subject study, the conversion of waste to carbon, water, oxygen, and nitrogen was emphasized. However, the ultimate goal of the waste conversion program is closure of the ecological life support system by converting waste to plant nutrients and other useful materials for extended planetary missions. The baseline of comparison considered for the catalytic technique is wet oxidation as defined by Johnson and Wydeven (1985). Wet oxidation has been under study for processing on-board spacecraft wastes for a number of years.

A strategy for upgrading petroleum-derived streams in a refinery is to add hydrogen or remove carbon, depending on the properties of the feedstock used and the products desired. The coking process utilizes high temperature to crack organic materials into carbon and lower-weight products. For example, the following model reaction represents this process:



Although actual systems are much more complex, the reactions reject carbon to yield a more hydrogen-rich product. The coking process also removes many impurities, such as suspended solids, salts, and sulfur. These impurities are concentrated on the coke, which is deposited in the coking reaction zone.

Oxidation uses oxygen or air to convert organic materials to carbon dioxide, water vapor, sulfur oxides, nitrogen or nitrogen oxides, and other low-yield oxide products. For example, cellulose oxidation yields water and carbon dioxide:



Although direct combustion may be possible, conversion is more effectively done using catalytic systems. Catalytic oxidation is extremely effective in applications where neither carbon monoxide nor flames can be tolerated. Use of catalytic oxidation also obviates the need for the high-pressure systems used for supercritical solvent-assisted oxidation. Catalytic oxidation systems can be designed to minimize equipment mass and require very little volume. Also, this process offers flexibility for the control of heteroatoms such as nitrogen. For example, a three-component control automobile catalyst system uses a two-stage conversion zone. The first stage is operated in an oxygen-deficient mode so that nitrogen oxides are reduced to nitrogen. The second stage is operated at a higher oxygen partial pressure to oxidize the remaining organic constituents, but at a temperature too low to re-form nitrogen dioxide.

Direct oxidation of waste streams will cause inorganic materials such as sodium chloride, calcium chloride, and magnesium chloride to be deposited onto the catalyst. This will eventually reduce catalytic activity and necessitate

replacement of the catalyst bed. Although the inorganic content of the waste stream sometimes is sufficiently low to permit direct oxidation, catalyst life is substantially enhanced by subjecting the waste stream to a coking reactor prior to oxidation. In the coking reactor, a large pore base (such as alumina substrate used for heavy oil catalysts) may be used to collect the carbon and solid products. This type of combined coker-oxidation process was studied in the subject investigation.

The catalytic process studied offers several potential advantages over the wet oxidation process. First, a portion of the carbon is removed from the waste and is directly deposited as a solid in the coker reactor. This carbon requires no further processing. In wet oxidation essentially all carbon is converted into carbon dioxide, which must be further processed to remove solid carbon material. Second, the coker and oxidizer reactions occur at atmospheric pressure, which facilitates use of lightweight reactor vessels compared to wet oxidation, which takes place at pressures above 1000 psi. Third, the coker and oxidizer vessels can be made considerably smaller than the wet oxidation vessel, if most of the wastewater is removed prior to coking.

An experimental program was carried out by the Signal Research Center (SRC), Des Plaines, Ill., as a subcontractor to AiResearch Manufacturing Company to characterize the coking process. No oxidation tests were run. Rather, a catalytic oxidation reactor design was formulated by SRC to process the output stream established from the coking experiment. The catalytic oxidizer design was based on extensive research and development experience gained by SRC in automotive emission control. Utilizing the basic process description results from SRC, AiResearch conducted a systems analysis to compare the relative merits of the catalytic process with the wet oxidation process for processing CELSS waste.

Based on the results of the study, considering the current state of development of the catalytic process, wet oxidation appears to be the preferred means to process CELSS waste. Three factors emerged from the study of the catalytic process that show the wet oxidation process to be more favorable. First, it was established that hydrolysis was necessary prior to coking to break down cellulose waste material to facilitate formation of a high-density solid carbon in the coker. The weight of the hydrolysis reactor negates the other weight advantages of the catalytic process. Second, it was established that the concentration of residual products in the liquid product stream from wet oxidation is sufficiently low that water in that stream can be separated by reverse osmosis. Because of the high solid and organic content in the hydrolysis product stream, water must be separated by a much more energy intensive distillation process in the catalytic process. Third, only 36 percent of the waste carbon was deposited as solid carbon in the coker. This yield was insufficient to offset the disadvantages of the catalytic process mentioned above.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

2.1 MATERIALS

2.1.1 CELSS Waste

The waste used for all studies was based on the CELSS model waste described by Wydeven (1983). Samples of Cerophyl, freeze-dried urine, feces, and food preparation waste were supplied by NASA for this study. Wash water and spent nutrient were prepared according to Wydeven (1983) using standard laboratory reagents.

For all experiments, a CELSS waste blend was produced according to the composition listed in Table 1 to give a final composition consisting of 14 wt percent solids. No analyses were performed on the waste components for carbon or nitrogen content. The values reported by Wydeven (1983) were used to estimate these compositions.

2.1.2 Coker Catalysts

Several different proprietary Universal Oil Products (UOP) alumina, aluminosilicate, zeolitic, and silica catalysts were used in the coking studies to evaluate their effect on coker solids residue densification. Table 2 summarizes the catalyst compositions. In general, varying the coker catalyst type had very little effect on the density of the final carbon residue.

2.2 APPARATUS

For this feasibility study, several different, separate apparatus were used to simulate different aspects of the CELSS treating process. The original program concept considered only coking of CELSS feed, followed by oxidation of the gases generated during the coking operation. During the course of the investigations, however, it was found that hydrolysis of the CELSS waste prior to coking was required in order to partially destroy the cellulosic structure of the waste and increase carbon residue density. The overall experimental procedure, then, comprised the following steps, which are schematically illustrated in Figure 1.

- (a) Hydrolysis of a 14 wt percent solids CELSS feed in a rocking autoclave under autogenous pressure to produce gases plus a solid/liquid residue.
- (b) Filtration and distillation of the solid/liquid residue to reduce the total volume of material charged to the coker apparatus. The filtration step isolated a solids component. Distillation of the filtrate produced a distillate fraction and a non-distillable bottoms fraction. The solids component and the bottoms fraction were combined and charged to the coker.
- (c) Coking of the solids and bottoms from the filtration/distillation step. The solids and bottoms were mixed with 48 cm³ of catalyst and

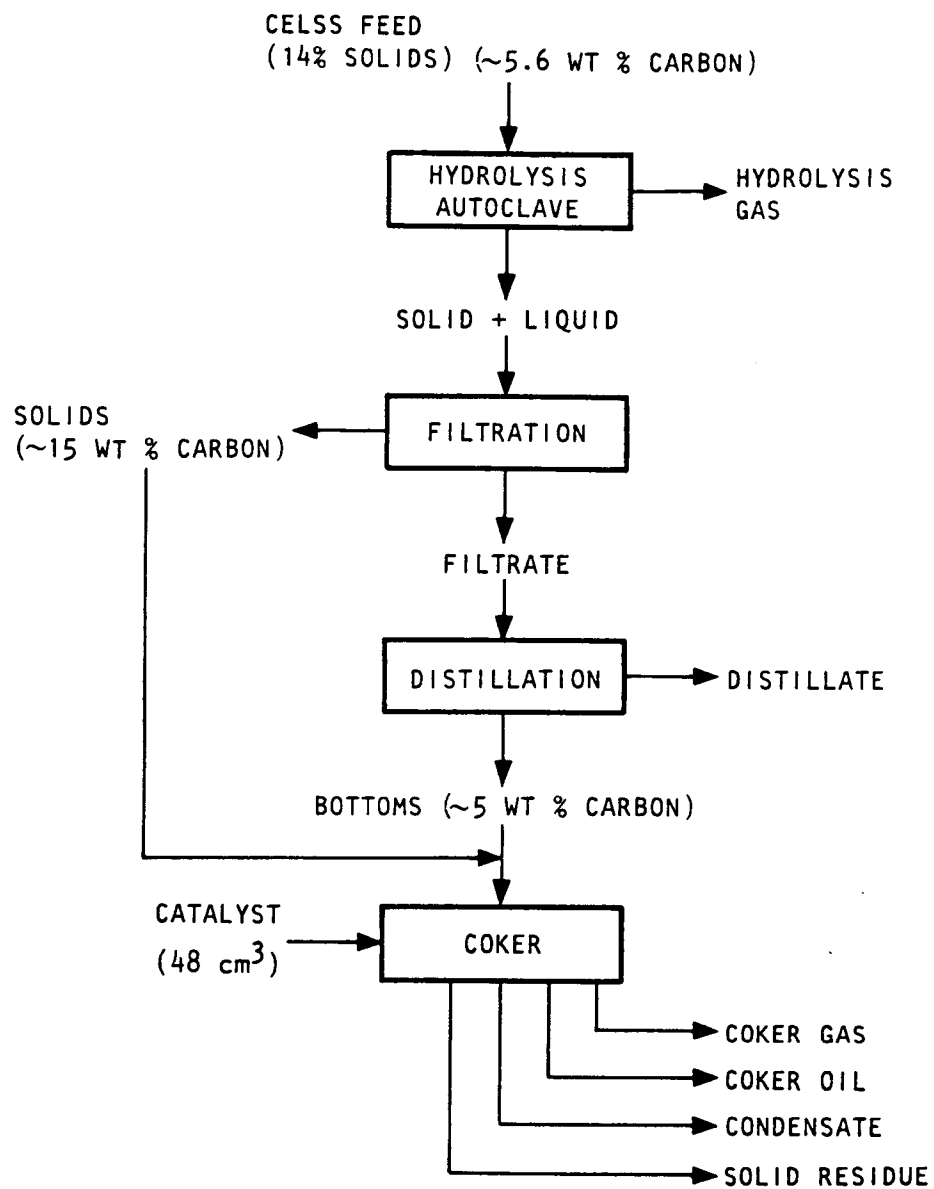
TABLE 1
COMPOSITION OF CELSS CHARGE*

Material	Total Wt, g	Carbon		Nitrogen	
		Wt%**	g	Wt%**	g
Cerophyl	67.4	40.63	27.38	4.21	2.84
Freeze dried urine	0.98	17.58	0.17	21.69	0.21
Freeze dried feces	0.675	41.92	0.28	8.26	0.06
Food prep.	0.264	43.93/43.55	0.12	2.40/2.8	0.007
Wash water	0.03	--	--	--	--
Spent nutrient	0.04	--	--	--	--
Totals	69.39	40.28	27.95	4.50	3.12

*Weights diluted with DI H₂O to 0.5 kg (i.e., 14 percent solids).
 **Analyses taken from Wydeven (1983).

TABLE 2
COKER CATALYST COMPOSITIONS

Catalyst	Composition	Porosity
SX143M-1	Silica gel	Control sample
DHC-2CB	Amorphous SiO ₂ -Al ₂ O ₃	High
DHC-8CB	" "	Medium
HC-100CEB	Zeolite	Low
DeH-4CB	Al ₂ O ₃	High
R-9CB	"	Medium
R-60CB	"	Low



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Figure 1. Schematic of Experimental Procedure

charged to the coker. The coking operation was done at atmospheric pressure and 450°C. It produced a solid residue, gases, coker oils, and a water condensate.

- (d) Catalytic oxidation of the gases produced from the autoclave and coking operations was not conducted due to limited resources. Instead a preliminary design was formulated based on the composition of materials to be charged to the oxidizer. This design was based on the extensive experience of Signal Research Center in the catalytic oxidation of gases in other commercial operations, including experience in the oxidation of automotive exhaust emissions.

2.2.1 Hydrolysis Autoclave

2.2.1.1 Apparatus

Pretreatment of CELSS waste materials by hydrolysis prior to coking was conducted in a 4-3/8-in o.d. rocking autoclave with 1800 cc capacity. The pressure vessel of this unit tilts through an angle of 30 degrees at 36 cycles per minute. The drive link is made separable to permit the reaction vessel to be turned head up for filling or head down for emptying.

2.2.1.2 Experimental Procedure

For all hydrolysis experiments, the following general procedure was utilized.

A 0.5 kg, approximately 500 ml, sample of CELSS waste (14 percent solids) was charged to the autoclave, including additives, if any. The autoclave was then capped, and the heaters and rocking assembly were turned on. Once the target temperature of 250°C was achieved (typically in about 60 to 70 minutes), conditions were maintained for 1 hour. During this time, pressure gauge readings indicated an internal autoclave pressure of between 600 and 700 psig.

After 1 hour, the heaters were turned off and the apparatus allowed to cool overnight. The vessel was then vented into a water displacement bottle to collect gas products from the reaction. The volume of gases was measured by displacement from the collection bottle with salt water into a wet test meter. A sample of the gas was also collected for analysis.

The autoclave was then uncapped, and its contents were poured into a collection bottle. The autoclave was washed with a weighed aliquot of wash water, and the washings were added to the collected liquid.

2.2.1.3 Operational Comments

Material balance was, in general, found to be difficult when using this apparatus. This was mainly attributed to the tendency of the apparatus to leak at elevated temperature and pressure, and to lines and valves which together contributed a significant dead volume relative to the volume of gas produced.

In evaluation of the results, it is assumed that all carbon and nitrogen not accounted for was lost as gas product of the same composition as that collected.

2.2.2 Filtration/Distillation

2.2.2.1 Apparatus

The product from the autoclave was filtered in a Buchner funnel using a water-generated vacuum to draw the liquid out of the solids captured on the filter paper. This resulted in the formation of two fractions, a solid and a filtrate.

The filtrate was charged into a distillation apparatus which consisted of a 500-cm³ round bottom distillation flask heated by an electric resistance heater. The vapors were passed into a condenser, and the condensate was captured in a 1-L round bottom flask.

2.2.2.2 Experimental Procedure

The filtrate from the Buchner funnel was charged, in portions, to the distillation flask. A thermometer was extended down into the liquid to measure the temperature of the liquid bottoms. When a temperature of 105°C was registered on the thermometer, the distillation was stopped.

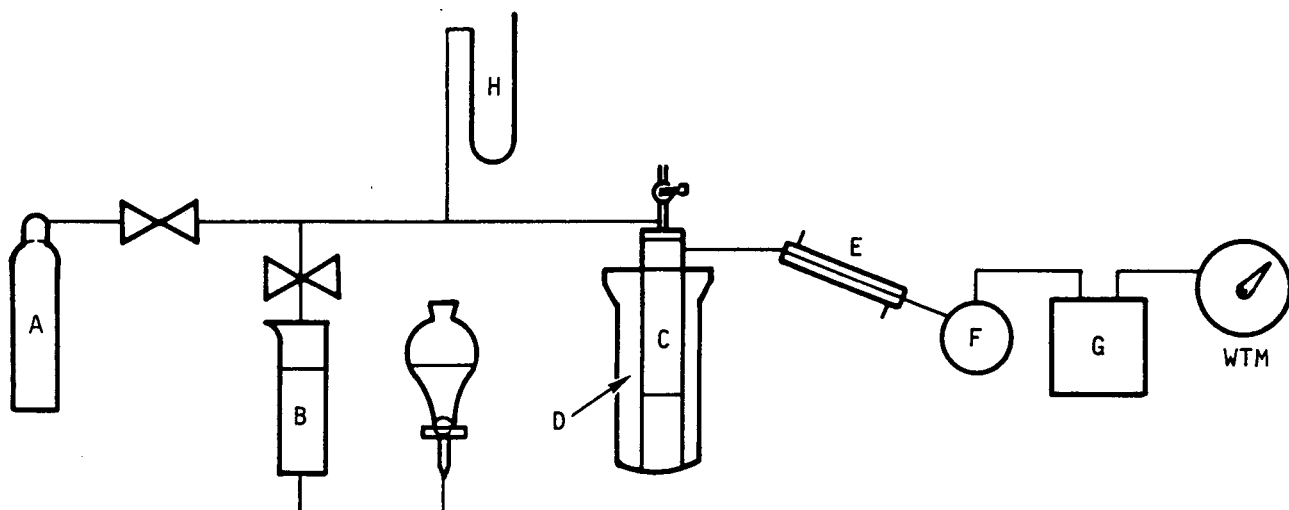
At this point, the filtrate had been separated by distillation into two fractions, a bottoms fraction and the distillate fraction. In order to ensure that light ends (low molecular weight gaseous hydrocarbons, typically butane and lighter) were not being lost to the atmosphere, the exit gases from the receiver were passed through a dry ice (-71°C) condenser. No significant amounts of material were ever collected in this trap. The condensate was weighed and sampled for carbon content by the Leco carbon method, and then discarded.

The solids from filtration were then combined with the bottoms from the distillation, and this mixture was charged to the coking apparatus. Total mass of the mixture typically was 80 to 100 gm, of which 18 to 20 percent by weight was carbon.

2.2.3 Coking

2.2.3.1 Apparatus

The coking apparatus (Figure 2) consisted of a 1-L cylinder of argon gas (A) feeding through a valve into either the coker (C) or the measured gas reservoir (B). A water manometer (H) measured the pressure developed in the system. The coker (shown in more detail in Figure 3) was a capped piece of pipe. The coker had a ball valve to add charge during a run if this was desired. The coker was heated by a block furnace (D) that had an automatic temperature controller. The exit gases vented into a condenser (E), and the condensate and gases passed into a separator (F) where water and tars were retained while the gases passed into a displacement reservoir (G). The displacement reservoir (G) allowed a measurement of the volume of the gases



- A: ARGON GAS CYLINDER
- B: GAS RESERVOIR (FOR CALIBRATION)
- C: COKER
- D: BLOCK FURNACE
- E: CONDENSER
- F: SEPARATOR (LIQUID COLLECTION FLASK)
- G: PRODUCT GAS RESERVOIR
- H: WATER MANOMETER
- WTM: WET TEST METER

Figure 2. Coking Apparatus

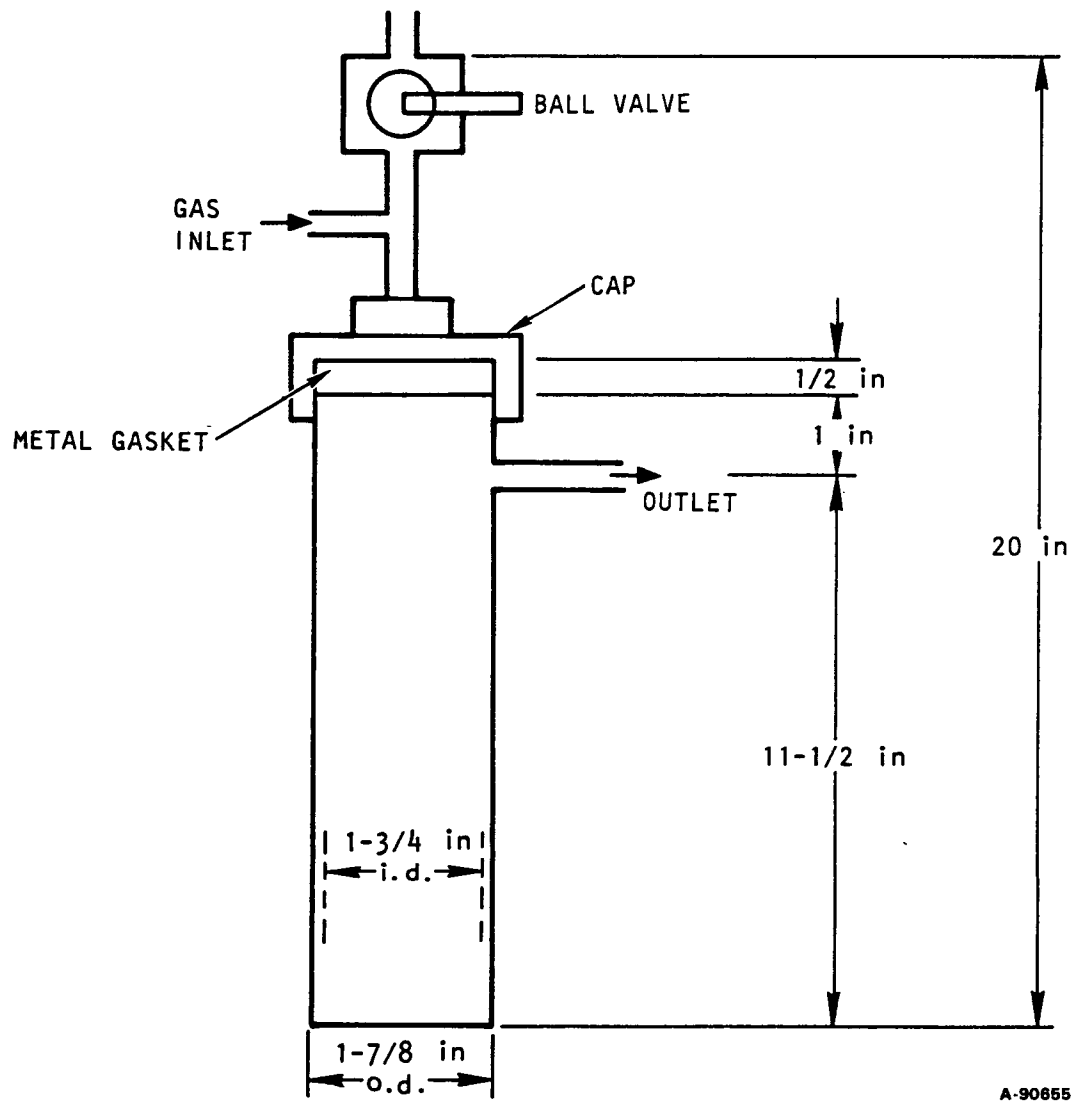


Figure 3. Coker Schematic (Not to Scale)

without passing those gases through a wet test meter (WTM), thus avoiding an analytical problem. The gases collected in the reservoir represented a sample of the total gas product, and so by pressuring out the gas through a gas sample tube an analysis of the total gas makeup could be obtained.

2.2.3.2 Experimental Procedure

The coker was charged with the mixture to be tested, consisting of the catalyst, the bottoms from the distillation of the filtrate, and the solids collected in the filtration step. The coker was closed up and placed in the furnace. After all of the lines had been connected, the system was tested for leaks by pressurizing it from the cylinder (A). If the pressure held, as measured by the manometer (H), the heater was turned on and the temperature allowed to rise to 300°C. This allowed a gradual vaporization of the water. After most of the water had come off, the temperature was raised to 450°C for one hour. At the end of this time, the apparatus was retested for leaks by passing a known volume of gas from the gas reservoir (B) through the apparatus. If the wet test meter and the gas volume did not agree, a leak was assumed. At the end of the run, the condenser (E) was heated with steam to melt and run all of the oils into the receiver (F). The receiver was disconnected, and the water phase was poured off, leaving a coker oil residue. The cooled coker was opened, and the contents scraped out.

3. EXPERIMENTAL RESULTS

3.1 INITIAL SCREENING EXPERIMENTS

3.1.1 Direct Coking of Cerophyl

During the initial phase of this study, preliminary experiments were conducted to assess the qualitative nature of solid residues which would be derived from coking of CELSS waste. For this purpose, a series of screening experiments were performed on the Cerophyl material itself, since this constitutes the major portion of the solids in CELSS waste.

These screening tests were very simply conducted by placing 100 cm³ of dry Cerophyl in a glass beaker, covering the beaker with aluminum foil to prevent combustion of the materials, and placing the beaker with its contents in a muffle oven at coking temperatures ranging from 300° to 600°C.

As the results in Table 3 indicate, direct coking of Cerophyl did not lead to an increase in density of the solid material. The apparent bulk densities (ABD) of the directly coked Cerophyl were the same or lower than the starting material regardless of coking temperature. On a carbon density basis (i.e., grams of carbon per cubic centimeter of volume) there was no net change via direct coking.

The skeletal density of the carbon residue was 1.6 g/cm³. Since one goal of this program was to produce a high-density carbon residue, it became apparent that some pretreatment of the Cerophyl prior to coking would be required to partially destroy the cellulosic structure of the material and thereby increase residue density.

3.1.2 Hydrolysis of Cerophyl

Hydrolysis of the Cerophyl was investigated as a means of destroying the structure of the waste. In the preliminary screening experiments, three types of hydrolysis were considered: enzymatic, basic, and acidic.

3.1.2.1 Enzymatic Hydrolysis

One experiment was conducted to evaluate the feasibility of enzymatic hydrolysis of Cerophyl utilizing cellulase enzyme. The initial result of this experiment showed no significant increase in carbon density, and this approach was not studied further.

3.1.2.2 Acid Hydrolysis of Cerophyl

Hydrolysis of Cerophyl with dilute sulfuric acid was investigated for potential benefits in densification after coking. Hydrolysis of 100 cm³ of Cerophyl with 2.86 g of sulfuric acid in 286 cm³ of water for one hour was conducted at temperatures ranging from 100° to 250°C. This was followed by coking at 400°C. As the results in Table 4 show, the density of the residue was not significantly increased by this means.

3.1.2.3 Caustic Hydrolysis of Cerophyl

Hydrolysis of Cerophyl with a dilute NaOH solution was investigated for potential benefits in densification after coking. Hydrolysis of 100 cm³ of Cerophyl with 2.86 g lye in 286 cm³ of water for one hour was conducted at temperatures ranging from 100° to 250°C. This was followed by coking at 400°C. As the results in Table 4 show, significant densification of residue occurred when the hydrolysis was conducted above 100°C. In subsequent experiments described below, it was also found that neutral hydrolysis (i.e., hydrolysis with no additives) produced residue densities at least comparable to caustic hydrolysis.

3.2 HYDROLYSIS AND COKING OF CELSS MODEL WASTE

The major area of effort in this study was the evaluation of the operating conditions and products obtained from hydrolysis and coking of the CELSS model waste material.

For all runs the initial charge of CELSS model waste consisted of a mixture of ingredients as outlined in Table 1 (Wydeven, 1983). The feed contained 69.39 g of dry solids per 500 g total feed, of which 27.95 g were carbon. The experimental procedures and apparatus used for this portion of the study were those described in Section 2 of this report.

A total of 11 runs were performed. Four of these runs (1 through 4) used no catalyst in the coking operation and were used to study the effects of different hydrolysis treatments. The remaining 7 runs (5 through 11) used neutral hydrolysis in every case and examined the effects of different coking catalysts.

TABLE 3
DIRECT COKING OF CEROPHYL*

Run	Muffle Temp., °C	Product ABD, g/cm ³	Carbon Density Wt % g/cm ³	
Cerophyl (as received)		0.42	40.6	0.17
A	300	0.29	62.1	0.18
B	400	0.23	61.0	0.14
C	500	0.30	64.2	0.19
D	600	0.36	64.5	0.23
E	300	0.33	59.0	0.20
F	400	0.31	54.4	0.17
G	500	0.21	60.0	0.13
H	600	0.34	58.0	0.20

*Conditions: 100 cm³ dry Cerophyl in muffle oven for 1 hour

TABLE 4
CEROPHYL HYDROLYSIS*

Run	Hydrolysis Temp., °C	Additive	Product ABD, g/cm ³	Carbon Density Wt % g/cm ³	
I	100	H ₂ SO ₄	0.25	NA	NA
J	150	H ₂ SO ₄	0.33	NA	NA
K	200	H ₂ SO ₄	0.25	NA	NA
L	250	H ₂ SO ₄	0.42	NA	NA
M	100	NaOH	0.33	50.8	0.167
N	150	NaOH	0.91	46.6	0.424
O	200	NaOH	0.59	NA	NA
P	250	NaOH	0.73	43.9	0.320

*Conditions: 100 cm³ Cerophyl + 286 cm³ H₂O + 2.86 g H₂SO₄ or NaOH; 1 hour hydrolysis + 1 hour coking at 400°C

The results of all runs are summarized in Tables 5 through 9. Table 5 shows the distribution of carbon by weight in each of the six product streams (refer to Figure 1). The compositions of the gases produced during hydrolysis are listed in Table 6. The compositions of the gases produced from the coking operation are shown in Table 7. Analysis of coker oils is summarized in Table 8. The densities and carbon percentages for the coked solid residues are summarized in Table 9.

3.2.1 Runs Without Catalyst

Experimental Runs 1 through 4 evaluated the effects of different hydrolysis treatments of the feed on product distribution. No catalyst was used during the coking operations.

Run 1 consisted of direct coking of the CELSS waste with no hydrolysis pretreatment. Runs 2, 3, and 4 utilized hydrolysis at 250°C under acidic, caustic, and neutral conditions, respectively. In general, similar amounts and types of products were produced in all cases. Runs using hydrolysis pretreatment tended to result in slightly lower amounts of carbon in the solid residue relative to the direct coking run, and this was primarily due to the formation of some additional gases during the hydrolysis step.

The major differences between the results of these runs were in the bulk densities of the solid carbon residues, as shown in Table 9. The solid residue produced by direct coking had an ABD of 0.53 g/cm³ (Run 1). Acid hydrolysis did not significantly increase density (Run 2). However, as indicated earlier, caustic or neutral hydrolysis did cause a significant increase in solid density. Caustic hydrolysis resulted in the highest ABD of 0.94 g/cm³ (Run 3), while neutral hydrolysis resulted in an ABD of 0.83 g/cm³. It is interesting to note that the carbon percentage for the solid residues was 45 to 46 percent for all samples except the caustic hydrolysis run, which was only 32.9 percent carbon. On a carbon density basis, the neutral hydrolysis condition resulted in the greatest densification (0.378 g carbon per cubic centimeter). For comparison, Cerophyl had an ABD of 0.42 g/cm³ at 40.6 wt percent carbon, giving a carbon density of 0.17 g/cm³ (Table 3). On a carbon density basis, therefore, neutral hydrolysis followed by coking results in a solid which is 2.2 times more dense than dry solid waste.

Gases produced during hydrolysis consisted entirely of carbon dioxide and carbon monoxide in a 97:3 mole ratio (Table 6). Coker gases were predominantly carbon dioxide and carbon monoxide, with lesser amounts of hydrogen, methane, and light hydrocarbons (Table 7). Coker oil represented a significant fraction of total carbon. It contained approximately 75 percent carbon, 3.5 percent nitrogen, and less than 10 ppm aromatics (Table 8). The carbon that carried over into the water distillate and coker condensate was not analyzed for hydrocarbon type.

3.2.2 Runs With Catalyst

The results from the baseline runs that did not utilize a coking catalyst indicated that the solid with the highest carbon density was obtained by using a neutral hydrolysis pretreatment. Therefore, a neutral hydrolysis step was

TABLE 5
HYDROLYSIS AND COKING OF CELSS WASTE--CARBON SUMMARY

(Initial Charge: 27.95 g Carbon)

Conditions		Amount of Carbon in Products, g							
Run	Hydro- lysis	Coker Catalyst	Hydro- lysis Gas	Distil- late	Coker Gas	Coker Oil	Coker Conden- sate	Coker Solids	Total Carbon
1	None	None	--	--	NA	8.44	1.62	12.39	22.45
2	H ₂ SO ₄	None	0.61	1.95	NA	4.14	0.95	11.39	19.04
3	NaOH	None	0.57	2.29	2.99	8.74	0.98	7.93	23.50
4	Neutral	None	NA	NA	2.36	5.55	0.94	10.28	19.13
5	Neutral	Silica control	0.51	1.13	1.70	8.16	0.90	9.02	21.42*
6	Neutral	HC-100	NA	1.61	0.78	3.11	0.67	13.15	19.32
7	Neutral	DHC-8	1.00	1.61	NA	1.28	1.09	10.83	15.81
8	Neutral	DHC-2	0.79	1.97	0.003	6.90	0.92	10.11	20.69
9	Neutral	R-60	0.85	1.02	NA	9.58	2.28	8.49	22.22
10	Neutral	R-9	NA	0.88	1.05	7.06	1.69	10.20	20.88
11	Neutral	DeH-4	0.87	1.41	1.61	8.36	1.20	8.58	22.03
Average, g			0.74	1.54	1.50	6.29	1.16	10.00	21.23
Average, % of Total			3.49	7.25	7.07	29.62	5.46	47.10	100
If assume all lost carbon is in hydro-lysis gas, then:									
Average, g			7.46	1.54	1.50	6.29	1.16	10.00	27.95
Average, %			26.71	5.51	5.37	22.52	4.15	35.80	100

*Carbon balance across hydrolysis was 79.8 percent.
Carbon balance across filtration/distillation was 98.2 percent.
Carbon balance across coker was 97.6 percent.
Overall carbon balance was 76.6 percent.

TABLE 6
HYDROLYSIS GAS COMPOSITION

Run	Total Moles	CO, Mol. %	CO ₂ , Mol. %	Carbon, g
1	NA	NA	NA	NA
2	0.051	2.7	97.3	0.61
3	0.047	3.2	96.8	0.57
4	NA	NA	NA	NA
5	0.043	19.4	80.6	0.51
6	NA	NA	NA	NA
7	0.083	4.8	95.2	1.00
8	0.065	2.6	97.4	0.79
9	0.071	3.6	96.4	0.85
10	NA	NA	NA	NA
11	0.072	4.1	95.9	0.87
Average	0.062	5.77	94.23	0.74

TABLE 7
COKER GAS COMPOSITION
Mole % by Component

Gas	Run							Average
	3	4	5	6	8	10	11	
H ₂	3.9	1.8	5.8	7.0	5.4	2.8	6.3	4.7
CH ₄	6.9	6.6	14.6	4.7	10.6	7.2	12.3	9.0
CO	19.6	6.0	8.6	7.0	9.0	8.4	9.4	9.7
CO ₂	57.5	74.4	57.1	75.7	57.8	69.4	52.2	63.4
C ₂ H ₆	4.7	3.8	7.9	1.6	6.0	4.2	7.5	5.1
C ₂ H ₄	0.8	0.6	1.3	0.8	1.0	0.8	1.2	0.9
C ₃ H ₈	2.4	2.4	2.8	0.8	3.2	2.5	4.1	2.6
C ₃ H ₆	0.8	0.8	1.1	0.8	1.4	0.8	1.4	1.0
C ₄ H ₁₀	1.3	1.2	0.4	0.0	1.6	1.4	1.9	1.1
C ₄ H ₈	1.0	1.0	0.2	0.8	1.8	1.1	1.8	1.1
C ₅ H ₁₂	0.5	0.6	0.0	0.0	0.8	0.6	0.7	0.5
Heavy hydrocarbons	0.6	0.8	0.2	0.8	1.4	0.8	1.2	0.8
Total moles	0.214	0.168	0.125	0.065	0.0001	0.074	0.109	0.108
Carbon, g	2.99	2.36	1.70	0.78	0.003	1.05	1.61	1.50

TABLE 8
COKER OIL COMPOSITION

Run	Weight, g	Carbon, percent	Nitrogen, percent	Carbon, g	Nitrogen, g
1*	11.0	76.7	3.50	8.44	0.385
2	5.6	74.0	3.54	4.14	0.198
3	11.1	78.7		8.74	
4	7.4	75.0		5.55	
5	10.8	75.6	3.86	8.16	0.417
6	4.0	77.8		3.11	
7	1.7	75.3		1.28	
8	9.2	75.0		6.90	
9	12.9	74.3	3.76	9.58	0.485
10	9.5	74.3		7.06	
11	11.0	76.0		8.36	
Average	8.6	75.7	3.67	6.48	0.371

*Aromatics analysis showed less than 10 ppm aromatics.

TABLE 9
COKER SOLID RESIDUE COMPOSITIONS

Catalyst			Coke Solid Residue					
Run	Type	Weight, g	ABD, g/cm ³	Total Wt., g	Carbon, %	Cat.-free Wt., g	Cat.-free % Carbon	Carbon, g/cm ³
1	None	--	0.53	26.7	46.4	26.7	46.4	0.246
2	None	--	0.54	24.5	46.5	24.5	46.5	0.251
3	None	--	0.94	24.1	32.9	24.1	32.9	0.309
4	None	--	0.83	22.6	45.5	22.6	45.5	0.378
5	SiO ₂	26.1	0.98	46.0	19.6	19.9	45.3	0.188
6	HC-100	30.0	1.09	52.8	24.9	22.8	57.7	0.274
7	DHC-8	16.1	0.94	45.3	23.9	29.2	37.1	0.226
8	DHC-2	17.7	0.75	36.1	28.0	18.4	54.9	0.211
9	R-60	23.0	1.13	52.7	16.1	29.7	28.6	0.177
10	R-9	23.3	0.94	44.9	22.7	21.6	47.2	0.212
11	DeH-4	12.6	0.66	31.9	26.9	19.3	44.4	0.179

used for all subsequent runs to determine whether the carbon density could be further improved by the presence of a catalyst. For all runs, a constant catalyst volume of 48 cm³ was used.

Run 5 utilized a standard silica gel material as a baseline reference case. This run was also used to perform a detailed carbon balance across each step of the experimental procedure, as well as an overall carbon balance. Of particular concern was the autoclave hydrolysis step since the apparatus used for this procedure was suspected of leaking gaseous products.

Results of the carbon balance for this run confirmed these suspicions. The carbon balance across the hydrolysis step was 79.8 percent. Carbon balances across filtration/distillation and coking steps were 98.2 percent and 97.6 percent, respectively. In order to conserve analytical costs, subsequent runs analyzed product streams only, and any carbon mass losses were assumed to be losses of hydrolysis gas of the same composition.

A comparison of all catalyst runs, whether the catalyst was silica, zeolite, aluminosilicate, or alumina, showed strikingly similar results in terms of types and distributions of products formed. Furthermore, the products produced in all the catalyst runs were very similar to those derived from the experiments which did not use any catalyst. The mass of carbon remaining as solid residue ranged from 8 to 13 grams (29 to 46 percent). All runs produced coker oils of similar composition. The variations in the amount of oils produced may be real, or may be simply a function of experimental run-to-run reproducibility. The compositions of both the hydrolysis and coker gases were also very similar. The amounts of carbon in the distillate and coker condensate water streams showed little variation. The total weight of residue deposited on the catalysts was also quite consistent, not only among different catalysts, but also when compared to non-catalytic residues.

The presence of catalyst during the coking operation also appeared to have little effect on the final density of the solid carbon residue. As the data in Table 9 indicate, the total weight of solids deposited on the catalysts was similar for all runs and not significantly different than the amount of solids deposited during runs which did not use catalyst.

To further evaluate any potential benefits of coking with the use of a catalyst, calculations were performed to estimate the theoretical maximum life and maximum carbon densities that might be reasonably expected to be achieved. For purposes of this calculation, it was assumed that for all catalysts the solid residue produced would have a true density of 1.5 g/cm³ at 45 wt percent carbon. It was further assumed that the coked solid residue would be capable of filling not only the intra-particle pore volume of the catalyst but also the interparticle void spaces which result from a packed, fixed bed of catalyst particles. The results of these calculations are shown in Table 10. This analysis indicates that the maximum carbon density is obtained using a neutral hydrolysis with no catalyst during the coking operation (Run 4). Since none of the catalyst systems caused an increase in carbon density relative to a noncatalytic operation, it is obvious that the addition of a catalyst would only serve to occupy volume which could otherwise be occupied by solid residue. Therefore, this conclusion is not surprising in view of the experimental results.

TABLE 10
ESTIMATE OF COKER CATALYST LIFE AND MAXIMUM
CARBON DENSITY

Run	Maximum Carbon,* g/cm ³	Maximum Dry Solid/Catalyst,** g/cm ³	Maximum CELSS/Catalyst,*** kg/cm ³
1	0.246	--	--
2	0.251	--	--
3	0.309	--	--
4	0.378	--	--
5	0.313	2.39	1.65
6	0.309	1.65	1.14
7	0.348	2.19	1.51
8	0.343	2.36	1.63
9	0.345	2.76	1.91
10	0.344	2.32	1.61
11	0.371	2.98	2.06

*Assumes coke is 1.5 g/cm³ density at 45 wt percent carbon.
Coke completely fills catalyst pores plus interparticle voids.

**This study used 69.46 g dry solids per 48 cm³ catalyst = 1.45 g/cm³.

***Assumes 7 percent solids in CELSS waste stream.

3.2.3 Nitrogen Product Distribution

The distribution of nitrogen among the various product streams was also examined for the hydrolysis and coking of CELSS model waste. For this purpose the liquid and solid products from Run 5 (silica reference run) were analyzed for total nitrogen content by the chemiluminescence (Antek) method. Based on the carbon product distribution results for all 11 runs, which showed very little variation in product stream composition with process changes, and in order to conserve analytical costs, it was assumed that the nitrogen distribution for each run would also be similar. In addition, as will be discussed below under the oxidation catalyst section, the form of nitrogen to be fed to the oxidation catalyst is not critical for complete conversion of all nitrogen species to molecular N₂. Product gas streams from hydrolysis and coking were not analyzed for nitrogen due to interference from atmospheric N₂ (from air and N₂ blankets) which would render these analyses suspect in terms of analytical accuracy. Also, the problems experienced with gas leaks during the hydrolysis autoclave runs, as had been determined from attempts to obtain carbon balance results, indicated that nitrogen gas analyses could be unreliable.

To substantiate the hypothesis that nitrogen distribution in the various product streams would not vary significantly between runs, samples of the coker oil produced from Runs 1, 2, 5, 9, and 11 were analyzed for nitrogen content for comparison purposes. As these results indicate (Table 8), these coker oils did not show a significant variation in percent nitrogen. Values ranged from 3.50 to 3.86 wt percent nitrogen, with an average value of 3.67 percent. No attempt was made to determine the chemical form of the nitrogen.

The results of nitrogen analysis of the solid and liquid streams for Run 5, the reference run using silica coking catalyst, are summarized below.

<u>Run 5 Product</u>	<u>Nitrogen, g</u>
Distillate	0.59
Coker oil	0.42
Coker condensate	0.76
Coker solids	<u>0.42</u>
Total	2.19

The overall nitrogen balance across hydrolysis, filtration/distillation, and coking was 2.19 g versus a CELSS waste charge of 3.12 g (Table 1) or 70.2 percent. The deviation from the total nitrogen balance is due to loss of some nitrogen compounds in such gaseous products as NO_x or ammonia (which were not analyzed) and to the lower accuracy of nitrogen analysis relative to that of carbon.

For purposes of this feasibility study, it is assumed that all nitrogen products that do not remain in the solid residue will be converted to N₂ during contact with the oxidation catalyst system to be described below. For Run 5, 0.42 g, or 13.5 percent, of the nitrogen in the waste remained in the coker solid residue.

4. OXIDATION CATALYST SYSTEM

The second major component of the catalytic waste conversion concept involves utilization of oxidation catalyst technology to convert volatile products from the coking operation to carbon dioxide, water, and nitrogen. This technology is based on extensive research and development activities in the automotive emission control area. Although no experimental work was done in this study to confirm the applicability of this technology to product streams from hydrolysis and coking, a reasonable estimate of catalyst type, size, and operating conditions may be obtained based on the composition of these materials.

4.1 FEED COMPOSITION

Table 11 summarizes a best estimate of the components to be fed to the oxidation catalyst system. This composition utilizes the average compositions which were experimentally determined in this study for the coker oil, coker gas, hydrolysis gas, and distillate and condensate streams. For purposes of

TABLE 11
COMPOSITION OF FEED STREAM GOING TO
OXIDATION CATALYST

Component	Coker Gas,* moles	Hydrolysis Gas,** moles	Nitrogen,*** moles	Total	Mol. %
H ₂	0.005			0.005	0.52
CH ₄	0.010			0.010	1.04
CO	0.010	0.038		0.048	5.00
CO ₂	0.068	0.592		0.660	68.77
C ₂ H ₆	0.006			0.006	0.63
C ₂ H ₄	0.001			0.001	0.10
C ₃ H ₈	0.003			0.003	0.31
C ₃ H ₆	0.001			0.001	0.10
C ₄ H ₁₀	0.001			0.001	0.10
C ₄ H ₈	0.001			0.001	0.10
C ₅ H ₁₂	0.0005			0.0005	0.05
Heavies	0.0009			0.0009	0.09
NO _x /NH ₃			0.223	0.223	23.24
Total moles	0.108	0.63	0.223	0.960	100.05
Moles carbon	0.125	0.63		0.755	
Moles nitrogen			0.223	0.223	

The feed stream to the oxidizer will also contain 0.52 moles of carbon in the form of volatile coker oils (Table 8), and 0.225 moles of carbon from distillate and coker condensate (Table 5).

*Average values from Table 7.

**Average values from Tables 5 and 6.

***Assumes all nitrogen in waste is converted to NO_x/NH₃.

this estimate, it is assumed that the hydrolysis distillate and coker condensate, which contain approximately 10 percent of the total carbon, will be passed across the oxidation catalyst in the vapor phase along with hydrolysis gas, coker gas, and the coker oil, also in the vapor phase. Such a scheme simplifies the overall number of treatment steps which might be required and, in particular, eliminates the need to utilize a water purification system for distillate and condensate.

The estimate for oxidation catalyst operation was based on a requirement to convert all carbon species completely to carbon dioxide and water and to completely convert all nitrogen-containing products to dinitrogen (N_2). For this estimate, it was assumed that all the nitrogen in the waste material would be converted to volatile nitrogen species in the form of NO , NO_2 , NH_3 or amines prior to the catalytic oxidation step. The precise form of nitrogen species is not critical to the overall operation of the oxidation catalyst; however, the ratio of oxidized nitrogen (NO_x) to reduced nitrogen (NH_3 , amines) would affect the overall requirements to add O_2 for complete conversion, as described below. In addition, the analytical nitrogen results (Section 3.2.3) indicated that approximately 13 percent of the waste nitrogen remained in the solid residue and, therefore, would not require processing over the oxidation catalyst. Therefore, the assumption that all nitrogen compounds require processing should represent a worst-case scenario in terms of oxidation catalyst requirements.

4.2 CATALYST CONDITIONS

In order to convert hydrocarbons to carbon dioxide and water, and also to convert all nitrogen-containing species to N_2 , a two-step catalytic process is envisioned. This two-step process comprises treatment of the feed over a first catalyst bed with just enough oxygen (or air) added to provide a stoichiometric "air/fuel" ratio, followed by treatment over a second catalyst bed with additional oxygen (or air) added. This two-step treatment is designed to give complete conversion of nitrogen compounds in the feed to dinitrogen (N_2) over a heavily loaded three-component control (TCC) catalyst in the first step.

The first reactor is loaded with a monolithic catalyst of 400 to 600 cells per square inch, a 2000-g γ -alumina washcoat, and active ingredients of platinum and rhodium at loadings of 150 and 50 g/ft³, respectively. This reactor volume should be sized to yield a gas hourly space velocity, based on the feed gas volume at 0° and 1 atm, of 15,000 hr⁻¹. The oxygen feed to the reactor should be metered and controlled relative to the feed rate and composition of the "fuel" to be exactly adequate to theoretically convert the fuel entirely to carbon dioxide, water, and nitrogen. Inadequate oxygen feed may result in production of some ammonia instead of N_2 , and some of that ammonia may be oxidized in the second reactor to nitric oxide and nitrogen dioxide. Excessive oxygen feed may result in the direct production of nitric oxide and nitrogen dioxide in the first reactor. This reactor should be operated using an inlet temperature of between 450° and 500°C.

The second reactor should be loaded with a catalyst similar to the first reactor except that the active ingredient is platinum at a loading of

200 g/ft³. A space velocity of 15,000 hr⁻¹ is also proposed for this reactor. The oxygen content of the feed gas to the reactor should be about 2 to 4 mole percent, and the catalyst temperature should be kept between 450° and 600°C.

Catalyst life should be at least 1000 hours with the clean feed described in Table 11 and with temperatures controlled to the ranges indicated here.

5. SYSTEMS DEFINITION AND COMPARISON

5.1 OBJECTIVE

Wet oxidation has been under study for a number of years as a means for processing on-board spacecraft controlled ecological life support system (CELSS) waste. Therefore it can be considered as a standard of comparison for waste processing systems. In this section a systems comparison is made between the subject catalytic (coker/oxidizer) waste processing system and wet oxidation. As an objective it was considered that both systems process waste to the basic constituents solid carbon, washwater-quality water, oxygen, and nitrogen.

Both the catalytic and wet oxidation processes yield a water and a gas product stream that require further processing. The chemical makeup of the product streams is not the same for the two systems. Thus to get a valid process comparison, it was necessary to expand the systems comparison to consider all the auxiliary components necessary to process the water and gas streams.

In the following subsections a basis for comparison of the two processes is established, overall systems are defined for the wet oxidation and catalytic processes, and components are sized to the extent necessary. Due to the limited scope of the subject contract, a complete systems sizing study was not carried out. Only sufficient detailed work was conducted to establish which of the two processes is the most competitive. In the current state of development, the wet oxidation process appears to be the most efficient process from the standpoints of simplicity and power considerations.

5.2 BASIS FOR THE SYSTEMS COMPARISON

The CELSS waste composition and generation rates defined by Wydeven (1983) were used in the systems comparison study. Components were sized for a six-man spacecraft. Waste component generation rates per man day are summarized in Table 12, which is reproduced from Wydeven (1983). The quantity of some major elements in the model waste are presented in Table 13, which is also reproduced from Wydeven (1983).

Processing systems were defined and sized to reduce the model waste to the basic components solid carbon, water, oxygen, and nitrogen. It was considered that water be processed to meet the washwater processing standards defined by the National Academy of Sciences, National Research Council (NAS/NRC, 1971). An abbreviated summary of these requirements, taken from Putnam (1976), is presented in Table 14.

TABLE 12
COMPOSITION OF CELSS MODEL WASTE*

Constituent	Weight, g/man/day	
	Dry	Wet
Urine	64	1,640
Feces	44	104
Inedible biomass**	4,400	17,400
Food preparation	20	60
Washwater	17	16,800
Spent nutrient	26	29,100
Total	4,500	65,200
Percent solids	6.9	--

*Source: Wydeven (1983).

**Inedible biomass was simulated by Cerophyl.

TABLE 13
AMOUNTS OF SOME MAJOR ELEMENTS IN THE MODEL WASTE*

Element	Amount, g/man (day)
Carbon	1,820
Hydrogen	251
Nitrogen	202
Potassium	184
Phosphorus	19.7
Sodium	18.4

*Using average elemental composition of the two batches of food preparation waste (from Wydeven, 1983).

TABLE 14
TENTATIVE STANDARDS FOR WASH WATER

<u>Physical Parameters</u> Color, cobalt units Conductance, specific, mho-cm ⁻¹ at 25°C Foaming Odor	≤15 ≤2000 Nonpersistent more than 15 sec Unobjectionable
<u>Chemical Constituents</u> Carbon, total organic, mg/L Detergents Lactic acid, mg/L Nitrogen, ammonia, mg/L Oxygen demand, chemical, mg/L pH Sodium chloride, mg/L Solids, dissolved, at 180°C, mg/L Urea, mg/L	≤200 Not specified ≤50 ≤5.0 Not specified 5.0 to 7.5 ≤1000 ≤1500 ≤50
<u>Microbiological</u> Microorganisms, number per ml, standard 48-hr plate count	≤10

Where possible, low-power techniques such as reverse osmosis will be used to renovate water streams. Rejection characteristics of a thin film composite (TFC) membrane suitable for washwater processing are presented in Table 15. These results, which will be used to evaluate water processing for the wet oxidation process, were measured for AiResearch by the Signal Research Center.

Some required six-man CELSS constituent processing rates were calculated based on the information presented in Tables 12 and 13 to assist in component sizing. These results are presented in Table 16. Similar rates established by AiResearch for Space Station are also presented for comparison. For the CELSS study, the waste feed rate is taken directly from Table 12 and multiplied by 6 to reflect a six-man generation rate. The carbon feed rate is obtained in a similar manner from the information in Table 13. The carbon dioxide and oxygen processing rates presented were obtained by assuming that

TABLE 15
TFC MEMBRANE REJECTION CHARACTERISTICS
WITH SYNTHETIC WASHWATER

	<u>Feed, ppm</u>	<u>Permeate, ppm</u>	<u>Rejection, %</u>
Na ⁺	38.7	3.1	92
K ⁺	11.6	1.5	87.1
Cu ²⁺	0.64	<0.01	99
Zn ²⁺	3.6	0.025	99.3
Cl ⁻	37.6	<1	>98
SO ₄ ²⁻	22.1	<1	95
Urea	10		>60*
Soap (sodium lauryl sulfate)	109.7		
Total organic carbon	55	14	74.6
Electrical conductivity	220 mho/cm	21-33 mho/cm	
pH	4.4	6.5 - 6.8	
Saybolt color	+28	+30	

*Probably on the order of 70 percent.

all carbon is converted to carbon dioxide, which is essentially the case for wet oxidation processing. The electrolysis water processing rate is obtained by assuming that the carbon dioxide is reduced to carbon and water, for example in a Bosch reactor, and the water is electrolyzed to produce hydrogen and oxygen.

The space station 304 lb/day/6 man wastewater feed is generated from laundry, dishwasher, shower, and handwash sources. As reflected in Table 12, a somewhat smaller washwater rate, 222 lb/day/6 men, is included in the CELSS feed stream. The carbon, carbon dioxide, oxygen, and electrolysis water rates shown for the Space Station in Table 16 are associated with processing in the closed-cycle metabolic oxygen system, rather than generation from waste products. Wash water on the Space Station will be renovated by either multifiltration or reverse osmosis. The purpose for presenting the Space Station processing rates in Table 16 was to show a relative size comparison, and to illustrate that existing on-board Space Station processing systems are too small to accommodate processing products from CELSS waste.

TABLE 16
COMPARISON OF CELSS AND SPACE STATION
PROCESSING RATE REQUIREMENTS

Item	CELSS, lb/day (6 men)	Space Station, lb/day (6 men)
Wastewater feed rate	861	304*
Carbon dioxide	88	13.2**
Carbon	24	3.6**
Oxygen	64	14.5**
Electrolysis water	72	16.3**

*Wastewater only.

**Processing requirement for closed metabolic oxygen supply system.

5.3 BASELINE WET OXIDATION SYSTEM

The baseline description for the wet oxidation process considered was taken from Johnson and Wydeven (1985). In that study CELSS waste described in Wydeven (1983) was processed under a range of operating conditions. The primary operating condition developed was processing for 1 hour at 275°C and 1500 psia with excess oxygen. Runs were made both with and without catalysts. Carbon and nitrogen balance data for product streams are reproduced in Table 17 from Johnson and Wydeven (1985) for a run without catalyst and a run with ruthenium catalyst. As can be seen, the ruthenium catalyst substantially enhanced the process. With the ruthenium catalyst considerably more carbon dioxide is generated and considerably less organic and nitrogen products remain in the product water.

The performance data for the run with ruthenium catalyst in Table 17 was taken as the basis for defining a total wet oxidation processing system. As will be shown, because of enhancement due to the catalyst, the hydrocarbon and nitrogen product concentrations in the product water are sufficiently low that the water can be processed with two stages of reverse osmosis. This type of processing is much more energy efficient than distillation, which is an alternate method. Without the ruthenium catalyst, six stages of reverse osmosis would be required, which is not nearly as desirable.

TABLE 17

MATERIAL BALANCE FOR CARBON AND NITROGEN WITH AND WITHOUT A CATALYST AT 548 K
AND 1500 psig FOR 1 HOUR (400 psig O₂ AT AMBIENT TEMPERATURE)

	No Catalyst	Ruthenium Catalyst
Percent carbon recovery in products		
CO ₂ in gas phase	61.7	73.8
CO ₂ in solution	9.6	11.0
Total carbon in solution (excluding CO ₂)	17.6	1.6
CO in gas phase	5.8	1.0
CH ₄ in gas phase	<0.03	4.8
Total carbon recovered	94.8	93.1
Percent nitrogen recovery in products		
NH ₃ in solution	58.2	2.4
N ₂ in gas phase	13.6	78.0
Organic nitrogen in solution*	9.3	0
Nitrate in solution	6.1	4.6
Nitrite in solution	0.12	ND**
Nitrogen in solid residue	0.44	ND
N ₂ O	<0.3	0.9
Total nitrogen recovered	87.8	85.9
Filtrate pH	6.4	4.6

*Results of the analysis for organic nitrogen were not meaningful since the amount of total Kjeldahl nitrogen found was consistently less than the amount of ammonia nitrogen.

**ND = not determined.

The concentrations of mineral ions and hydrocarbon and nitrogen compounds in the product water were estimated by assuming that the mass of product water was equal to the mass of feed water; i.e., no evaporative loss. Further, it was assumed that all mineral ions in the feed remained in the product water. Thereby, data presented in Tables 12, 13, and 17 were combined to provide the concentration estimates presented in Table 18.

Any reverse osmosis processing of the product water will be done in a batch mode. In a batch mode feed concentrations increase steadily as water is passed through the membrane. Since membrane rejection factors remain relatively constant during this time, more impurities are passed during the latter phase of the batch process when their feed concentrations are higher than during the initial phase. To get average permeate concentrations, it is necessary to calculate constituent batch concentration reduction factors by performing an integration on transfer of impurities over the feed concentration range of processing.

TABLE 18

SELECTED ESTIMATED CONCENTRATIONS IN THE
PRODUCT WATER FROM WET OXIDATION

Constituent	No Catalyst		Ruthenium Catalyst	
	g/man (day)	ppm	g/man (day)	ppm
Carbon	338	5568	31	511
Ammonia	163	2685	7	115
NO ₃	62	1021	48	790
Potassium	184	3031	184	3031
Phosphorus	19.7	325	19.7	325
Sodium	18.4	303	18.4	303

Such batch reduction factors for selected constituents in solution in the product water from wet oxidation with ruthenium catalyst (Table 18) were evaluated using rejection factors from Table 15. These results are presented in Table 19 for reverse osmosis processing to a 5-percent residual. Also presented are the initial concentrations, and concentrations after one and two stages of reverse osmosis processing. With the exception of ammonia, the constituents shown are within the allowable range for the water standard selected (Table 14) after two stages of processing. Additional sorption or ion exchange could be used to bring the ammonia concentration within specification if necessary. This analysis establishes that reverse osmosis can be used to process the wet oxidation product water instead of much more energy intensive evaporative techniques.

TABLE 19

REVERSE OSMOSIS PROCESSING ESTIMATES
FOR WET OXIDATION PRODUCT WATER

Constituent	Membrane Rejection	Batch Reduction*	Concentration		
			Initial	First Stage	Second Stage
Carbon	0.75	0.55	511	281	155
Ammonia	0.75**	0.55	115	63	34
NO ₃	0.90**	0.27	790	213	58
Potassium	0.87	0.34	3031	1031	350
Phosphorus	0.90**	0.27	325	88	24
Sodium	0.92	0.22	303	66	15

*For batch processing to 5 percent residual.

**Estimated rejection factors.

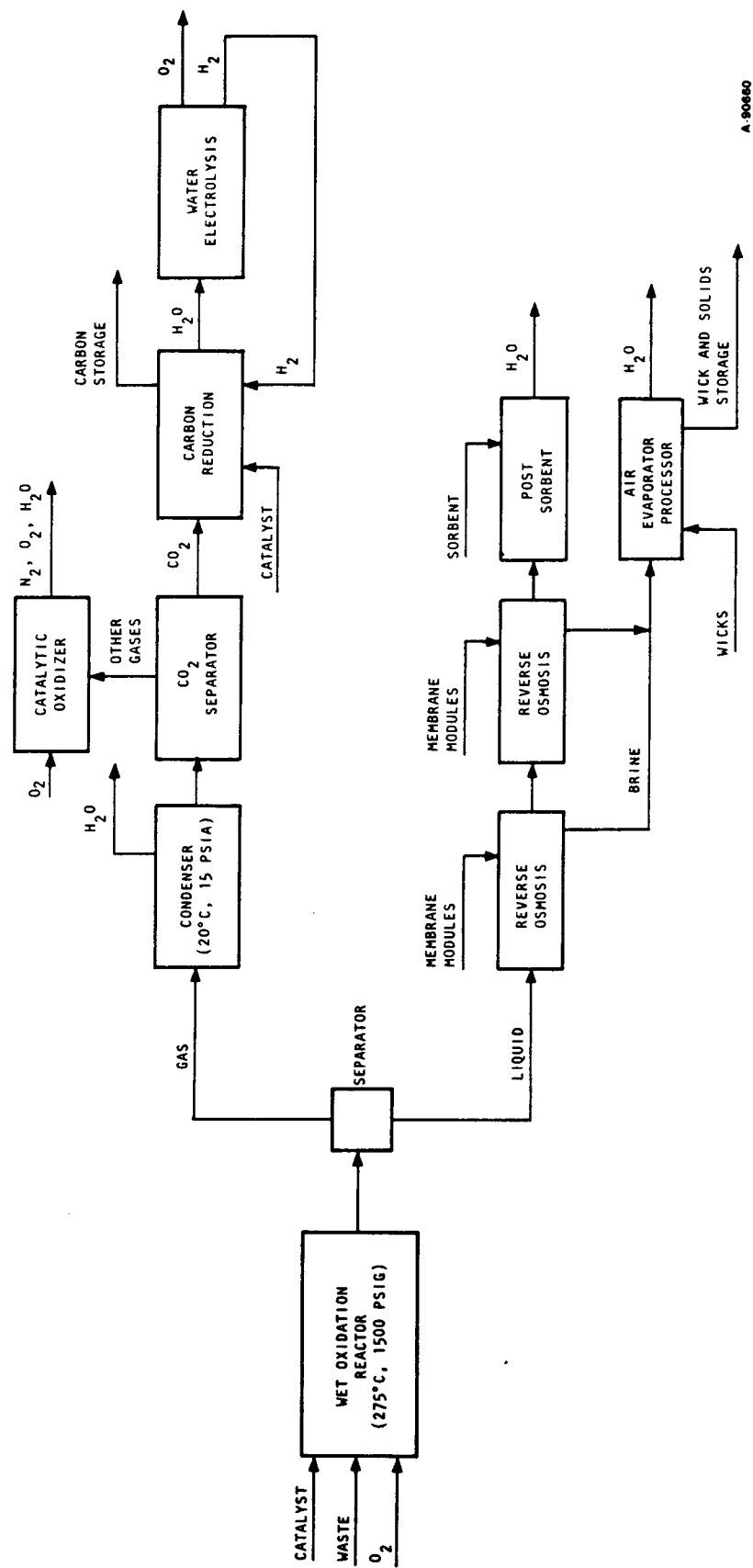
A process flow diagram is presented in Figure 4 for a wet oxidation system to process CELSS waste. The process is amenable to either batch processing or continuous-flow processing, which was utilized in the development test unit described by Jagow (1975).

After wet oxidation (Figure 4), the liquid and gaseous products are separated. The liquid is processed by two stages of reverse osmosis. Brine is further completely processed by an air evaporation system with solids being deposited in expendable wicks which are totally dried. After water removal, carbon dioxide is separated from the gas stream. The residual gas is directed through a catalytic oxidizer to dispose of undesired nitrogen and hydrocarbon compounds, and vented into the cabin. The carbon dioxide is then reduced to solid carbon and water. The water is electrolyzed to separate out oxygen.

As mentioned earlier, the wet oxidation process shown in Figure 4 is amenable to and probably best operated as a steady-flow process. Recuperative enhancement of the wet oxidation reactor is a logical addition for a steady-flow process, as shown in Figure 5. Very little or no power input would be required to run the wet oxidation reactor in this mode. An 80 to 90 percent heat recovery can be assumed for the recuperator. Since the wet oxidation process is exothermic, it may be possible that the process itself can supply the remaining heat required.

Weight, volume, and power sizing estimates were made for the carbon dioxide separator, carbon reducer, and electrolysis unit, which will be used later for system comparison. Nearly all the carbon in the CELSS feed is converted to carbon dioxide for the ruthenium catalyst processing baseline (Table 17) for the system shown in Figure 4. Approximately three-fourths of this carbon dioxide will be processed by the gas flow branch shown in Figure 4. The remaining carbon dioxide will be discharged into the cabin and be processed by the cabin closed-cycle metabolic oxygen system. That system will have to be sized to accommodate this additional contribution from waste processing. To simplify estimating the weight, volume, and power of the necessary carbon dioxide processing equipment, it was assumed that combined values for the gas stream components, shown in Figure 4, and the enlargement necessary for the cabin carbon dioxide processing components can be approximated by sizing the components shown in Figure 4 to process all the carbon dioxide generated. It was further assumed that there is 100 percent conversion of carbon to carbon dioxide.

Using these assumptions, the weight, volume, and power requirement estimates presented in Table 20 were generated. To generate these results it was assumed that a zeolite four-bed molecular sieve was used for carbon dioxide separation, a Bosch reactor was used for carbon reduction, and a solid polymer electrolyte static feed system was used for electrolysis. The values shown in Table 20 were then obtained by scaling from smaller units of similar design sized by AiResearch for the Space Station. In keeping with established techniques for scaling system component sizes, weight, volume and power were scaled proportional to the 0.7 power of process flow rate for the molecular sieve and Bosch units. The electrolysis unit is of a modular construction, so it was scaled proportional to the process flow rate.



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Figure 4. Wet Oxidation system for Processing CELSS Waste

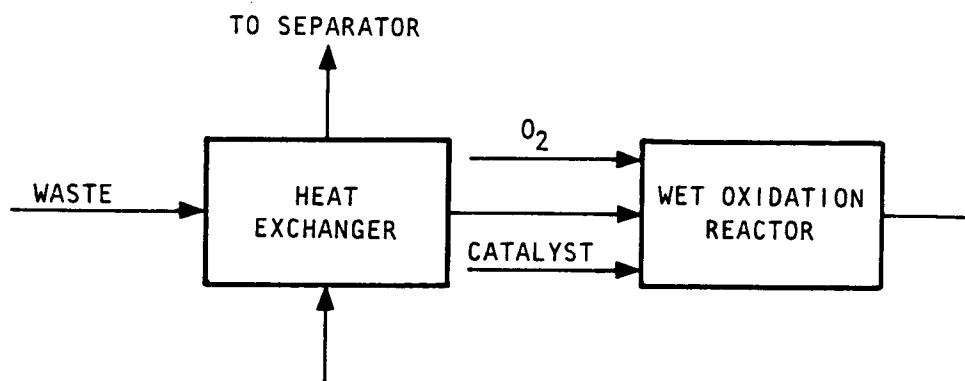


Figure 5. Recuperative Enhancement for Steady-Flow Wet Oxidation processing

TABLE 20
SIZE OF GAS PROCESSING COMPONENTS
FOR THE WET OXIDATION SYSTEM

Component	Weight, lb	Volume, ft ³	Power, W
Four-bed molecular sieve	126	7	399
Bosch reactor	1330	69	999
Solid polymer electrolysis unit	924	74	6466
	<u>2380</u>	<u>150</u>	<u>7864</u>

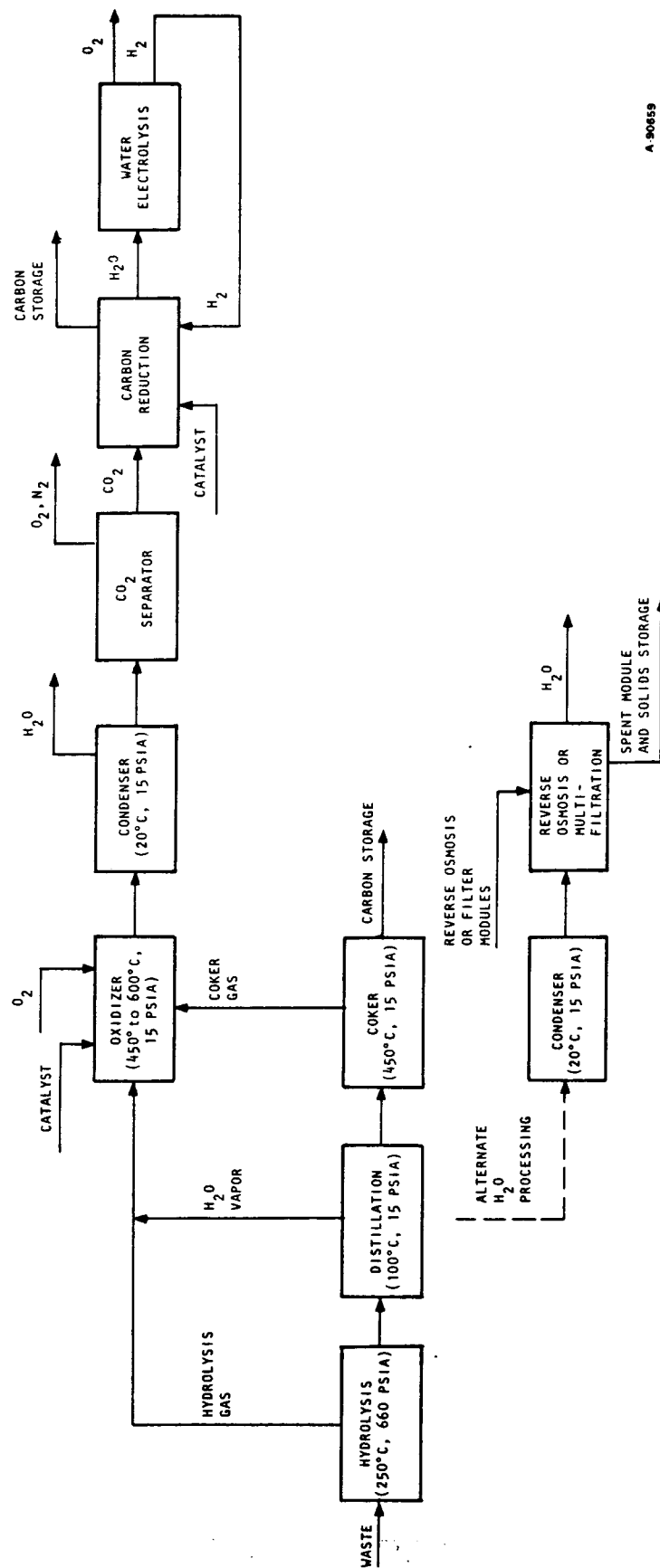
5.4 CATALYTIC SYSTEM FOR PROCESSING CELSS WASTE

The catalytic process flow diagram presented in Figure 6 was designed for processing CELSS waste based on test results presented in Sections 3 and 4. The system shown is designed to process waste to solid carbon, washwater-quality water, oxygen, and nitrogen. Waste material is first subjected to neutral hydrolysis at 250°C under autogenous pressure (600 psia) for one hour to break down cellulose material, which increases residual product density. Next, the bulk of the water in the waste is separated by distillation. Thereafter the residual material is coked at 450°C at ambient pressure for one hour. No catalyst is used in the coker. Solid carbon and mineral residues in the coker are deposited in a removable liner or tubes which can be extracted for storage. In practice, the distillation process and coking process will have to be combined in the same reactor vessel to avoid material handling difficulties which would be associated with moving dried waste material into a separate coker.

Hydrolysis gas, water vapor, and coker gas are directed to a catalytic oxidizer where hydrocarbon and nitrogen compounds are converted to carbon dioxide, water, nitrogen, and oxygen at 450° to 600°C and ambient pressure. Water is removed by condensation, followed by carbon dioxide removal. Oxygen and nitrogen are vented into the cabin. Thereafter the carbon dioxide is reduced to solid carbon in a Bosch reactor. Product water is electrolyzed to separate oxygen.

The lower portion of Figure 6 shows an alternative, less energy-intensive method of processing the waste distillate. Here the distillate is condensed and processed by reverse osmosis or multifiltration. Distillation is necessary for water removal prior to water treatment by reverse osmosis because of the very high organic content of the hydrolysis water. The hydrolysis product is a virtual "organic soup." Direct reverse osmosis or multifiltration treatment of this water would be very inefficient and would also require some type of filter press operation with all its attendant mechanical and material handling complexities.

Examination of Figure 6 reveals that the catalytic process is not readily amenable to steady-flow operation. Distillation at 100°C must occur prior to coking. Coking then initiates at 100°C, but is enacted at higher temperatures, up to 450°C. No easy way can be envisioned to flow the waste material through a zero-gravity processing cell, first as an increasingly viscous 100°C slurry, and then as a higher temperature solid to be deposited at a high density in removable tubes or a liner. Relegation to batch processing puts the catalytic process at quite a disadvantage with respect to energy efficiency. It is not readily possible to utilize a recuperator to recycle heat from the water condenser to evaporate liquid from the incoming waste in batch mode processing. Thus, full power penalties must be paid, first to evaporate the water and then for heat rejection to condense the water.



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Figure 6. Catalytic System for Processing CELSS Waste

5.5 SYSTEM COMPARISON

For comparing the catalytic process (Figure 4) to the wet oxidation process (Figure 6), it will be assumed that the alternate reverse osmosis water processing technique shown in Figure 6 is applicable to process the hydrolysis distillate. Comparison of Figures 4 and 6 shows a good deal of similarity between the two systems. The catalytic processing system offers the advantage that approximately 36 percent of the carbon in the CELSS waste feed is directly converted to a solid and does not have to be processed in the gaseous carbon dioxide processing branch. An energy balance and component comparison will be made in this section that shows this savings is not large enough to offset the higher power requirement and increased complexity of the catalytic process, however.

By a component-to-component comparison between Figures 4 and 6, it can be seen that the hydrolysis and distillation/coker reactors in Figure 6 are analogous to the wet oxidation reactor of Figure 4. These two component sets are probably about comparable in weight, but the hydrolysis and distillation/coker combination is probably larger in volume. The wet oxidation reactor will be much more energy efficient (particularly in the recuperative mode), since it does not have to vaporize the wastewater. The wet oxidation reactor is also probably simpler in design.

The liquid processing branches of both processes are quite similar. The wet oxidation system has two stages of reverse osmosis, compared to the catalytic system, which probably requires only one stage. The catalytic processing system requires a condenser, however.

The gas processing branches of the two systems require the same five processing components. The components for the catalytic process will be 36 percent smaller, however, which reflects its 36 percent smaller carbon dioxide processing rate. This potential savings is quantified in Table 21, based on the component size data presented previously in Table 20.

TABLE 21
POTENTIAL SAVINGS IN THE CARBON DIOXIDE PROCESSING
COMPONENTS WITH THE CATALYTIC PROCESSING SYSTEM

Process	Total Component Specifications		
	Weight, lb	Volume, ft ³	Power, W
Wet oxidation	2380	150	7864
Catalytic	1523	96	5032
Potential savings	857	54	2832

Relative energy requirements for the wet oxidation and hydrolysis-distillation/coker reactors are presented in Table 22. The powers presented are calculated for heatup and vaporization of the 801 lb/day (33.4 lb/hr) wastewater flow that makes up 93 percent of the CELSS waste. Heat addition to raise waste temperature above 100°C is considered to be fully recovered by flash evaporation upon depressurization for the situations that involve distillation. Heat addition to raise solids to the coker process temperature is considered negligible compared to heat for water processing because of the relatively small solids mass.

TABLE 22
COMPARISON OF HEAT REQUIREMENTS
FOR THE WASTE PROCESSING SYSTEMS

System Comparison	Heat Requirement, kW
<u>Relative to wet oxidation without recuperation</u>	
Catalytic (hydrolysis and distillation)	10.86
Wet oxidation (without recuperator)	- 4.45
Catalytic CO ₂ processing savings*	- 2.83
Net additional for catalytic process	<u>3.58</u>
<u>Relative to wet oxidation with 90% recuperative heat recovery</u>	
Catalytic (hydrolysis and distillation)	10.86
Wet oxidation (with recuperator)	- 0.44
Catalytic CO ₂ processing savings*	- 2.83
Net additional for catalytic process	<u>7.59</u>
<u>Relative to wet oxidation with distillation</u>	
Catalytic (hydrolysis and distillation)	10.86
Catalytic CO ₂ processing savings*	- 2.83
Wet oxidation (with distillation)	-10.86
Net savings for catalytic process	<u>(2.83)</u>

*From Table 21.

The power requirement for the catalytic process is compared in Table 22 to that required for three wet oxidation configurations: wet oxidation without recuperator enhancement, wet oxidation with recuperator enhancement, and wet oxidation with product water processing by distillation. For the first two cases the catalytic process requires more power than wet oxidation, even after considering the net savings to the catalytic process from processing less carbon dioxide. This situation arises because the catalytic process requires distillation processing of the wastewater, while more efficient reverse osmosis can be utilized to process wet oxidation product water. If the solid carbon yield were increased from 36 to 81.5 percent, the power requirements for the two processes would be equal for wet oxidation without recuperation. Even with 100 percent solid carbon conversion, the catalytic process cannot compete with the wet oxidation process with recuperation.

In the third comparison in Table 22, the catalytic process is compared to wet oxidation on a more even basis, where wastewater is processed by distillation in both techniques. Such a wet oxidation system was proposed by Jagow (1975). In this case the catalytic process has a 2.83-kW advantage due to its 36 percent solid carbon conversion yield. Higher solid carbon yields would increase this advantage.

6. CONCLUSIONS

Two processes were evaluated for their potential feasibility to catalytically process spacecraft controlled ecological life support system (CELSS) waste. The objective was to provide sufficient data on a coking/oxidation concept for waste treatment to conduct a preliminary systems comparison with the wet oxidation technique. These goals were completed. In the current state of development, wet oxidation appears to be the preferred process from the standpoint of both component simplicity and power requirement. Detailed conclusions of the study are the following:

- (a) Results from coking experimental studies indicated that none of the catalysts employed in the coking operation caused a significant increase in solid residue density relative to a non-catalytic operation. A hydrolysis pretreatment of the waste prior to coking did result in increased densification of the coked solid residue. Hydrolysis under neutral or caustic conditions was found to be most beneficial for densification.
- (b) Products obtained from the hydrolysis and coking steps included a solid coked residue, gases, water condensate streams, and a volatile coker oil. The solid residue contained 36 percent of the waste carbon and 13 percent of the waste nitrogen. The water product streams from hydrolysis distillation and coker condensate contained approximately 10 percent of the total carbon and 43 percent of total nitrogen. Volatile oils produced during coking contained 23 percent of the total carbon and 13 percent of total nitrogen. Gaseous products from hydrolysis and distillation consisted primarily of carbon dioxide, carbon monoxide, and light hydrocarbons and comprised approximately 32 percent of the total carbon.

- (c) An estimate of oxidation catalyst size and operating conditions was made based on the measured product slate derived from the hydrolysis and coking operations. For estimating purposes, the feed to the oxidation catalyst system was assumed to include all hydrolysis gases, coker gases, coker oils, and water streams containing organics (all in the vapor phase). A two-stage reactor system was proposed to quantitatively convert all nitrogen species to dinitrogen (N_2) and to convert all carbon species to carbon dioxide and water.
- (d) The overall catalytic processing scheme evolved consists of coking of the waste feed at 450°C to produce a solid residue and volatile hydrocarbons, nitrogen species, and water. All volatile materials are directly fed to a two-stage oxidation catalyst system operating between 450° and 600°C with injection of oxygen or air. A hydrolysis step was utilized preceding the coking operation to increase the density of the solid carbon residue formed during coking. It is more energy efficient to separate most of the water by distillation after hydrolysis and process it by multifiltration or reverse osmosis, rather than heating the water vapor to 450°C to process it in the oxidizer. Distillation separation is deemed necessary because of the high organic content of the hydrolysis product mixture.
- (e) It appears that the mineral and organic content of the wet oxidation product water is sufficiently low that this water can be separated by two stages of reverse osmosis. Reverse osmosis is a very energy efficient separation process compared to distillation. This situation provides an overwhelming energy advantage to wet oxidation.
- (f) Gas stream postprocessing components are very similar for both processes. Gas stream component sizes and power requirements are 36 percent smaller for the catalytic process, since 36 percent of the waste carbon was removed in coking. This savings is not sufficient to make up for the complexity and power penalty introduced by the need for water separation by distillation with the catalytic process.

7. RECOMMENDATIONS

An overwhelming factor in establishing the competitive advantage for the wet oxidation process is the apparent possibility that water can be separated from the wet oxidation product stream by reverse osmosis or multifiltration. It is recommended that the performance of this separation process be confirmed by test with an actual wet oxidation product stream. If such energy efficient separation is not possible, the results of the subject study will have to be reexamined in a new light.

Another key area warranting further study is the chemistry and mechanisms involved in densification of the waste during coking. Results from this study indicate that destruction of the cellulose three-dimensional structure is a

key factor, and various hydrolysis treatments of the waste at elevated temperatures prior to coking had a beneficial effect. Additional studies would be useful in order to optimize this process to give maximum densification with minimum energy requirements. Combined with this should be considered alternative catalyst systems to be used during coking operations to further densify the residue, as well as to reduce the amount of volatile hydrocarbons produced. While the catalysts surveyed in this program showed no beneficial effects on densification, it is very probable that new catalysts could be designed specifically for this process which would have a significantly improved performance.

A second processing area which warrants further investigation is the use of catalytic oxidation technology for waste processing. Any further development of this proposed system would require testing of real waste volatiles on the proposed "three component control" catalysts to more precisely define operating conditions and catalyst life. As part of such a study, a more detailed analysis of potential catalyst poisons (such as sulfur and phosphorus) need to be defined and evaluated. Depending on the amount and nature of such potential poisons, optimum oxidation catalysts can be designed to meet the specific requirements of space station waste conversion.

8. REFERENCES

Jagow, R. B., "Design, Fabrication, and Testing of a Wet Oxidation Waste Processing System," Contract NAS1-11748, Bioengineering Organization, Lockheed Missiles and Space Company, Sunnyvale, Calif., May 15, 1975.

Johnson, C. C., and T. Wydeven, "Wet Oxidation of a Spacecraft Model Waste," SAE Paper 851372, presented at the Fifteenth Intersociety Conference on Environmental Systems, San Francisco, Calif., July 15-17, 1985.

National Academy of Sciences, National Research Council "Recommended Tentative Standards for Wash Water in Manned Spacecraft," Panel on Water Quality for Manned Spacecraft, Advisory Center on Toxicology, December 1971.

Putnam, D. F., "Development Assessment of Wash Water Reclamation--Final Report," NASA CR 137934, August 1976.

Wydeven, T., "Composition and Analysis of a Model Waste for a CELSS, "NASA Technical Memorandum 84368, September 1983.

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16. Abstract Catalytic techniques were evaluated for processing waste products on-board space vehicles. The goal of the study was the conversion of waste to carbon, washwater-quality water, oxygen, and nitrogen. However, the ultimate goal is conversion to plant nutrients and other materials useful in closure of an ecological life support system for extended planetary missions. The resulting process studied involves hydrolysis at 250°C and 600 psia to break down and compact cellulose material, distillation at 100°C to remove water, coking at 450°C and atmospheric pressure, and catalytic oxidation at 450 to 600°C and atmospheric pressure. Tests were conducted with a model waste to characterize the hydrolysis and coking processes. An oxidizer reactor was sized based on automotive catalytic conversion experience. Products obtained from the hydrolysis and coking steps included a solid residue, gases, water condensate streams, and a volatile coker oil. Based on the data obtained, sufficient component sizing was performed to make a preliminary comparison of the catalytic technique with oxidation for processing waste for a six-man spacecraft. At the current state of development, wet oxidation seems to be the preferred technique from the standpoint of both component simplicity and power consumption.					
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